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CHEMISTRY OF ADHESION AT THE POLYIMIDE-METAL INTERFACE

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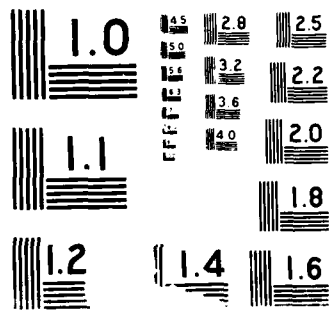
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## CHEMISTRY OF ADHESION AT THE POLYIMIDE-METAL INTERFACE

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### ABSTRACT

This article describes recent studies of the chemistry of adhesion between thin ( $d \geq 11 \text{ \AA}$ ) polyimide films and silver and copper substrates, and the structural changes in the polymer when polyamic acid is imidized to polyimide. The thin polyamic acid films were formed by vapor phase deposition of 1,2,4,5-benzenetetracarboxylic anhydride (PMDA) and 4,4'-oxydianiline (ODA) under high vacuum conditions and subsequent imidization by heating in vacuum. Both ODA and PMDA are at least partially dissociated upon adsorption onto clean copper and silver and with increasing film thicknesses react to form the polyimide precursor, polyamic acid. Heating to  $T \geq 425 \text{ K}$  leads to polymerization to form polyimide films which are thermally stable to about 700 K. Polyimide films with mean thicknesses as small as 1.1 nm have been fabricated in this way and their bonding to the substrate as determined by x-ray photoemission studies is summarized. Infrared reflection absorption data gives further evidence that the polyimide bonds to the substrate via fragmented PMDA. Changes in the surface topography and molecular structure of the films during imidization are demonstrated by scanning tunneling micrographs and infrared reflection absorption data.

### INTRODUCTION

Polyimides (PI) are high temperature polymers that have a unique combination of thermal stability, low dielectric constant, chemical inertness and easy processability into coatings or films. The most commonly used polyimides are those formed by the reaction of 4,4'-diaminodiphenyl ether (oxydianiline (ODA)) and 1,2,4,5 benzenetetracarboxylic anhydride (pyromellitic dianhydride (PMDA)). In microelectronic device applications [1-3], these are used in both packaging [1,4] and as insulating interlevel dielectrics [1,5].

The successful adhesion between PI and metals is essential in these applications and the physical and chemical factors which contribute to the adhesion are of fundamental interest. In the absence of extrafacial inhomogeneity (eg. stress free films) the strength of the adhesive couple is dependent directly on the physics and chemistry at the polymer/metal interface [6]. This has prompted a number of investigations to probe the microscopic origins of the adhesive bonding. Utilizing surface science techniques such as X-ray photoemission spectroscopy (XPS) and near edge x-ray absorption fine structure (NEXAFS), the electronic core and valence structure of PMDA-ODA polymer/metal interfaces have been studied [7-12]. Other techniques such as transmission electron microscopy [13], Rutherford backscattering spectroscopy [14] and electron energy loss spectroscopy [15,16] have also been utilized in the study of polymer/metal interactions.

Studies of thin metal films deposited on the surface of a much thicker (usually bulk) polyimide phase have provided the main source of chemical information [7-12,17]. For example, room temperature deposition of chromium leads initially to bonding to the PI substrate, possibly via the carbonyl groups, and subsequently with increasing chromium coverage to formation of a carbide like carbon species [18]. Similarly, other electropositive metals such as aluminum, [11] titanium [12] and nickel [7] also appear to react through this carbonyl entity. Copper [7,9,11] and silver [7], however, show

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only a weak interaction with the oxygen in the other part of the chain.

The second method for producing a metal/polyimide interface is spin coating or evaporating the polymer precursor (PAA) onto a supported metal film, prior to curing and the formation of polyimide. In the spin coating process the polyamic acid is dissolved in a polar solvent, e.g. N-methylpyrrolidone (NMP), whereas in the evaporation process both polymer constituents PMDA and ODA are deposited onto the substrate [19-21]. Bulk polyimide/metal interfaces formed in this way have been shown to produce a marked increase in, for instance, the peel strength of a PI/copper oxide interface compared to conventional metal deposition [17]. The precursor/metal interfacial reaction is apparently much stronger compared to that of the metal/PI interfacial reaction where the polymer is fully cured prior to metal deposition.

The presence of the polar solvent must also be considered in a comparison of spin coated and vapor deposited films. As demonstrated recently by Kim, et al. [17] and Kowalczyk, et al. [22] for polyimide/copper oxide interfaces, the presence of the solvent NMP leads to formation of cuprous oxide particles in the polymer film, whereas interfaces prepared by the solventless method, i.e. vapor deposition of the organic constituents or copper evaporation onto fully cured polyimide, showed no such precipitates.

The way the interface is prepared needs to be considered if any valid comparisons are to be made between the adhesion of different metals/polyimide interfaces. The fundamental variations between each type of interface will essentially reflect the electronic and therefore chemical properties of the bulk metals as compared to those of metal atoms, clusters or very thin metal films. However, the formation of the polymer (from the dissolved precursor or from the vapor codeposited constituents) will also play a significant role in determining the specific bonding.

This brief report is organized as follows. First, we summarize our previous results on the interaction of the pure polyimide constituents PMDA and ODA with clean silver and copper surfaces. Codeposition of PMDA and ODA leading to polyamic acid formation is discussed in relation to the adsorption of the pure constituents. As will be shown, imidization of polyamic acid films involves structural changes in the polymer film resulting in an average orientation of the polyimide chains parallel to the substrate. We finally show the first data on the topography of thin vapor-deposited polyimide films as determined from scanning tunneling micrographs.

## EXPERIMENTAL

Our experimental setup and the procedures to produce ultra-thin polyimide films by vapor deposition has been described in detail previously [21,23]. In brief, the constituents PMDA and ODA were deposited from heated quartz tubes in a UHV chamber onto the substrate held at room temperature, followed by heating in vacuum to imidize the film. The various stages of deposition and reaction were followed by x-ray photoelectron spectroscopy using a hemispherical electron energy analyzer (Leybold Heraeus EA11) operated with a resolution of 0.92 eV as measured on the Ag 3d 3/2 emission. The infrared data were recorded with a home-built vacuum IR Reflection Absorption Spectrometer with a grating monochromator and with a commercial FTIR Spectrometer (Mattson Cygnus 100). The IR data have been corrected for the transmission of the instrument so that relative intensities can be compared over the whole spectral range. The STM results at various deposition and curing stages were obtained with a Nanoscope (Digital Instruments NanoScope I) operated in air.

## RESULTS AND DISCUSSION

Both PMDA and ODA undergo fragmentation on clean polycrystalline silver and copper surfaces and on a Cu(111) substrate [20,23,24]. An important aspect for evaluating the possible bonding situation of polyamic acid and sub-

sequently polyimide with the metal substrates is the degree of dissociation, i.e. whether the fragments still retain functional groups which can react with ODA or PMDA to effectively interlink the polymer film with the substrate. The degree of fragmentation on the surface was determined from the XPS data by the C 1s, O 1s and N 1s binding energies and an evaluation of the stoichiometry of the surface phase, as discussed in detail in references [21,23]. A model for the bonding configuration of the molecular fragments consistent with the core level binding energies and the stoichiometry of the surface layer can be derived, but needs to be tested by direct structural probes. In the following we summarize our previous XPS data and show IR reflection absorption data for ultra-thin films of PMDA, ODA, polyamic acid and polyimide on polycrystalline copper which support our previous findings that polyimide adhesion occurs via a chemically bonded fragmented layer of PMDA and possibly ODA.

#### Adsorption of PMDA and ODA on Silver and Copper Surfaces

The XPS data taken for PMDA adsorbed on polycrystalline silver exhibited distinctive changes as a function of film thickness, i.e. monolayer to multilayer adsorption. The spectra taken for film thicknesses in excess of  $d \sim 11 \text{ \AA}$  clearly showed the expected binding energies and intensities for molecularly condensed PMDA. For monolayer coverages, however, the interpretation of the C 1s and O 1s band revealed a deficit of one CO moiety of PMDA, indicating the reaction of one anhydride functionality with the surface leading to the release of one CO molecule into the gas phase. Angular resolved XPS measurements further suggested a tilted bonding geometry of the PMDA fragment with respect to the substrate. The resulting model of PMDA adsorption on silver at room temperature is shown in Fig. 1. A tilted bonding geometry of the PMDA fragment has also been observed on a Ag(110) surface in a NEXAFS study [25].

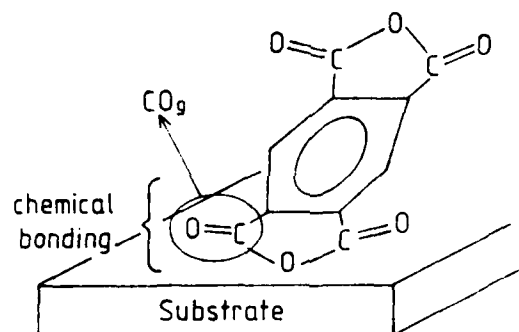


Figure 1. Proposed bonding model for PMDA on a polycrystalline silver surface.

The bonding for PMDA on silver is not fully understood but probably involves interaction of the oxygen atoms of one fragmented anhydride group in a monodentate or bidentate configuration and possibly of a carbon atom in the phenyl ring with the substrate. The bonding to the substrate is relatively strong, since heating the layer does not lead to desorption but to further decomposition [23]. This bonding configuration is such that the undisturbed anhydride group of the PMDA fragment can react with ODA and thus link a polyimide chain to the substrate. Indirect evidence for such a bonding configuration in the polyimide/metal interface has been obtained in our studies of ultra-thin ( $11 \text{ \AA} < d < 35 \text{ \AA}$ ) polyimide films on polycrystalline silver and copper surfaces. The O 1s data showed spectral features which are consistent with the interfacial presence of fragmented PMDA and ODA. Further support

for such a model was derived from the observation that pure PMDA and ODA layers undergo decomposition upon heating to temperatures necessary to imidize the polyamic acid, whereas in the case of thin polyamic acid films no evidence was found for a dissociative reaction in the interface. This result indicates that the PMDA (and ODA) fragments are thermally stabilized by the polyimide overlayer, which in turn means that a chemical bond must exist between interface and polymer film.

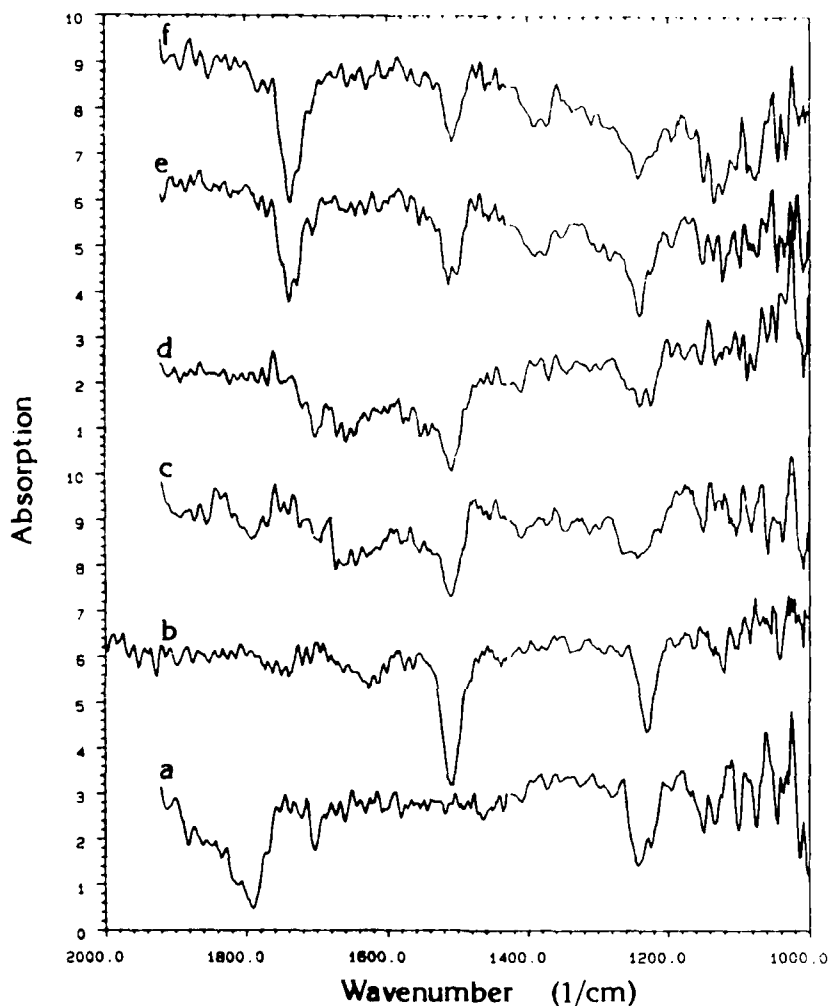


Figure 2. Infrared Reflection Absorption data with a polycrystalline copper substrate. a) PMDA,  $T = 300$  K; b) ODA,  $T = 300$  K; c) Codeposited ultra-thin film of PMDA and ODA,  $T = 300$  K; d) Film heated to 375 K for 15 min.; e) Film heated to 440 K for 15 min.; f) Film heated to 473 K for 15 min.

Whereas the stoichiometry of the PMDA surface complex on silver was well defined, our XPS experiments on copper indicated additional decomposi-



tion involving the loss of two carbonyl groups [24]. IR reflection absorption data for a thin film (1-2 monolayer) of PMDA on polycrystalline copper are shown in Fig. 2a. The spectra displayed were taken after dosing the substrate at 220 K and subsequently heating to 300 K. A comparison of the IR reflection absorption spectrum to that of bulk PMDA [26] or dissolved PMDA [27] reveals that the phenyl ring modes (expected at 1368  $\text{cm}^{-1}$  and 1460  $\text{cm}^{-1}$ ) are missing or very weak, whereas the symmetric and asymmetric carbonyl stretching modes at 1790  $\text{cm}^{-1}$  and 1860  $\text{cm}^{-1}$  (although in a different intensity ratio and not resolved as in the bulk compound) and the C-O-C anhydride stretching mode (or  $B_{2u}$  ring mode of the phenyl ring) at (1240  $\text{cm}^{-1}$ ) are present (see Table I). In addition, a small absorption band is observed around 1703  $\text{cm}^{-1}$ , which does not exist in the PMDA bulk spectra.

Table I

Expt ( $\text{cm}^{-1}$ )	Literature [27] ( $\text{cm}^{-1}$ )	Mode Assignments [30,31]
<b>PMDA</b>		
1085	1085	
1152	1152	
1240	1240	$\nu(\text{COC})$ stretch or ring mode ( $B_{2u}$ )
----	1368	Ring mode
----	1460	Ring mode ( $B_{2u}$ ) ( $\nu_{17}$ )
1703	----	Tentatively assigned to a C=O stretch in a formative type surface bond
1790	1770	Carbonyl $\nu(\text{C=O})$ stretch (sym)
1860	1858	Carbonyl $\nu(\text{C=O})$ stretch (asym)
<b>ODA</b>		
1110	1115	
1225	1225	$\nu(\text{COC})$ asym stretch or ring mode ( $B_{2u}$ )
1275	1282	
1325	1320	
1390	1380	
1510	1500	Ring mode ( $B_{1u}$ ) ( $\nu_{13}$ )
1625	1620	$\text{NH}_2$ scissor mode or ring mode ( $A_g$ ) ( $\nu_2$ )

In molecular PMDA, the phenyl ring and the anhydride groups are all in the plane of the molecule. Thus, if the molecule would physisorb in a configuration parallel to the surface, the in-plane phenyl ring modes as well as the carbonyl and anhydride stretching modes should not be detectable due to the dipole/image dipole cancellation of the effective dipole moment on the metal surface. For a configuration where the PMDA molecular plane is perpendicular or tilted with respect to the surface plane, the above mentioned modes should be active. However, our results show that only the carbonyl and anhydride modes are active, whereas the phenyl ring modes are not detected. This, consistent with the XPS results, reveals that the PMDA molecule must undergo fragmentation in the adsorbate phase, and the absence of the phenyl ring modes might even indicate that concurrent with the loss of carbonyl groups the phenyl ring opens due to a strong interaction with the metal substrate.

The present data are not sufficient to derive a bonding model, in particular since it is not obvious that the adsorbate phase is homogeneous. However, we want to point out some characteristic features. The decrease in the asymmetric carbonyl stretching frequency, when compared to the undissoci-

ated condensed molecules at 220 K [26] reveals that to some extent the anhydride functionalities, which include two carbonyl groups, are effected upon heating from 220 to 300 K. Secondly, we find a band at  $1703\text{ cm}^{-1}$  which is at a frequency where the carbonyl stretching frequency of formate species have been observed [28], indicating the possibility of a similar bonding situation for the fragmented PMDA molecule. Most importantly, however, the fragmented PMDA layer still contains anhydride functionalities as indicated by the  $1240\text{ cm}^{-1}$  C-O-C stretching frequency. These anhydride functionalities therefore are accessible to a reaction with oxidianiline. Heating the ultra-thin PMDA film to 373 K results in the loss of essentially all molecular vibrations [26]. This is consistent with XPS data, which show sublimation and further fragmentation of PMDA above room temperature.

Oxidianiline was found to decompose partly on both silver and copper surfaces at room temperature in our XPS studies. Contrary to PMDA on silver, where a defined surface species was isolated, ODA is adsorbed in a mixed phase possibly consisting of molecular ODA, dissociated oxygen and oxidianiline fragments [23,24].

The IR reflection absorption spectra of a polycrystalline copper surface with a 1-2 monolayer ODA film (Fig. 2b.) shows, albeit with different intensities than in the dissolved molecular compound [27], all molecular vibrations. Compared to the molecular spectra, the  $\text{NH}_2$  scissor at  $1625\text{ cm}^{-1}$  and  $\text{NH}_2$  stretching modes (not shown here) are very broad indicating possibly hydrogen bridge bonding to the surface oxygen (originating from partial dissociation of ODA) or within the adsorbate phase. The presence of all molecular vibrations furthermore indicates a structural and/or chemical non-homogeneous phase, as was also inferred from the XPS data.

#### Codeposition of PMDA and ODA: Polyamic Acid Formation and Imidization of the film

Codeposition of ODA and PMDA onto the metallic substrates held at room temperature leads to polyamic acid formation [20,21,23,24]. The film can contain excess PMDA and ODA molecules, depending on the flux of the two constituents, but the excess molecules will evaporate when the film is heated. In the imidization reaction, water is formed and released into vacuum. The XPS results showed that imidization of the film begins at  $T \sim 400\text{ K}$  as evidenced by a decrease in the hydroxyl O 1s band. However, in all our XPS experiments we were unable to produce a pure polyimide film. Spectroscopic evidence suggested that the films formed by vapor deposition always contain some unreacted or incompletely reacted oxidianiline molecules or fragments [21,23].

The XPS experiments on the formation of ultra-thin polyimide films ( $11\text{ \AA} < d < 35\text{ \AA}$ ) on silver and copper further revealed that the interface between the polyimide and the metal contains PMDA and/or ODA fragments which are stabilized against thermal decomposition by the presence of the polyimide film. If pure ODA or PMDA monolayer films are heated in vacuum above  $T \sim 470^\circ\text{C}$ , dissociation into carbonous species was observed.

The same conclusion, i.e. the stabilization of the interfacial layer of fragmented ODA and PMDA is derived from our IR experiments. The vibrational mode assignments are given in Table II. Fig. 2c shows the IR reflection spectrum of an ultra-thin codeposited layer of PMDA and ODA. Both the bands of molecular ODA and PMDA fragments are present, in addition to a more pronounced broad  $\text{NH}_2$  scissor mode band around  $1660\text{ cm}^{-1}$  and, not shown here, bands due to hydroxyl group formation around  $3600\text{ cm}^{-1}$ . Also, the band at  $1703\text{ cm}^{-1}$ , which is identified with fragmented PMDA on the surface, is visible. Heating the film results in more complete polyamic acid formation. The spectra taken at  $T = 373\text{ K}$  (Fig. 2d) of the same film are dominated by the ODA ring mode, a broad  $\text{NH}_2$  scissor mode region, and a persistence of the mode originating from fragmented PMDA at  $1703\text{ cm}^{-1}$ . Note that the carbonyl stretching frequencies are absent within the signal to noise level, indicating that in the thin polyamic acid film the dynamic dipole moments associated

with the carbonyl stretches must have a strong component parallel to the surface plane. At  $T > 425$  K, imidization sets in and leads to dramatic changes in the spectra. The bands at  $1117\text{ cm}^{-1}$  and  $1383\text{ cm}^{-1}$  are due to the imide  $(\text{OC})_2\text{N C}$  mode and imide C-N stretch, respectively. The strong increase in the carbonyl stretching frequency indicates a structural rearrangement in the film as compared to the polyamic acid film. Note that the PMDA fragment vibration at  $1703\text{ cm}^{-1}$  is persistent as a shoulder on the strong carbonyl band.

TABLE II

	PAA 25°C	PAA 100°C	PI 150°C	PI 200°C	Mode Assignments [30]
(1)	1085	1085	1082	1082	
(2)	1104	----	1100	----	
(3)	----	----	----	1125	1117 $(\text{OC})_2\text{N C}$ mode (imide)
(4)	1152	1152	1150	1150	
(5)	1245	1245	1245	1245	1252 Ether linkage $\nu(\text{COC})$ stretch (asym).
(6)	----	----	1385	1385	1383 $\nu(\text{C-N})$ stretch (imide)
(7)	1510	1510	1510	1508	1505 Ring Mode (ODA)
	1545	1545	1540	----	
	1625	----	----	----	
(8)	1700	1700	1705	----	
(9)	----	----	1738	1738	1725 Carbonyl $\nu(\text{C=O})$ stretch (sym)
	----	----	1770	1770	1779 Carbonyl $\nu(\text{C=O})$ stretch (asym)
(10)	1790	----	----	----	Carbonyl mode in polyamic acid
(11)	1860	----	----	----	Carbonyl mode in polyamic acid

The polyimide spectra (2e, f) show all the features of a fully cured polyimide film [19] and no indications for a substantial amount of isoimide formation. The same observation, i.e. that vapor deposited polyamic acid converts nearly quantitatively to polyimide, has been reported originally for thick films [19].

Our IR data thus reveal that spectral features associated with PMDA fragments in the interface persist when a thin polyamic acid film is imidized, and secondly, during imidization structural changes occur in the polymer film.

The average orientation of the polymer chain can be inferred indirectly by changing the polarization of the light with respect to the surface plane. In films where the thickness does not exceed the screening length of the metal electrons only those modes are detected in an IR reflection absorption experiment which have a component of their dynamical dipole moment perpendicular to the surface. In thicker films other modes will also be detected, yet their relative intensity ratio will still reflect the average orientation of their dynamical dipoles.

In Fig. 3 we show the IR reflection absorption spectra of a thick polyimide film taken with p-polarized light at an incidence angle of  $85^\circ$  with respect to the surface normal (3a) and a FTIR Reflection absorption spectrum with unpolarized light at an incidence angle of  $45^\circ$ . The relative polarization of the light can be changed by refraction effects at the polyimide/vacuum interface. This would change the direction of the p-component of the electric field vector in the polymer film to a larger angle ( $49^\circ$ ) with respect to the surface normal. This, however, does not alter the general model of the polymer orientation discussed below [26].

The FTIR spectrum is partially obscured by residual  $\text{CO}_2$  gas phase bands between  $1800$  and  $1500\text{ cm}^{-1}$ . Both spectra show the same bands, but the intensity ratio between the carbonyl stretching band ( $1725\text{ cm}^{-1}$ ), the ODA  $\nu_{13}$  ring modes ( $1505\text{ cm}^{-1}$ ) and the imide bands ( $1383\text{ cm}^{-1}$  and  $1117\text{ cm}^{-1}$ ) and the  $\nu_{\text{COC}}$

ODA mode is distinctly different. In spectrum 3a, only those vibrations with a dipole moment perpendicular to the surface will be detected, whereas in spectrum b, all dipole orientations should be active, since the incident light was not polarized.

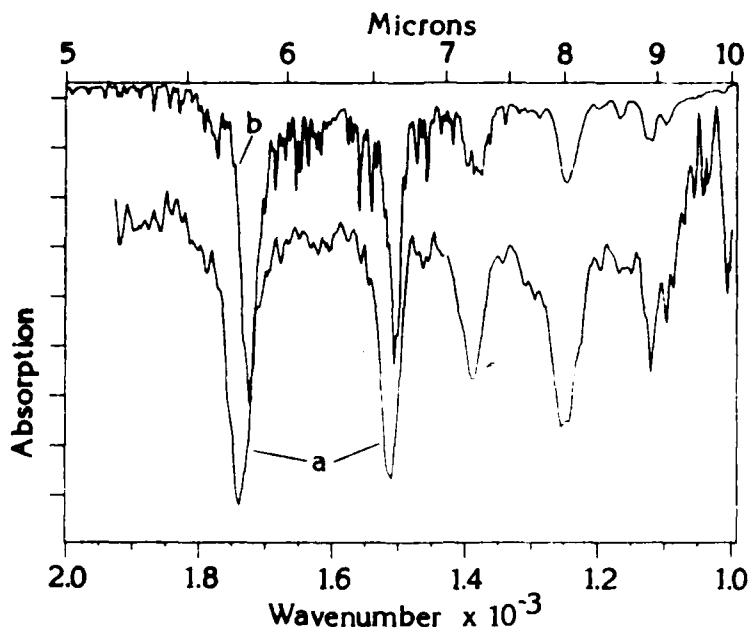


Figure 3. Infrared Reflection Absorption data for a polyimide film about 100 Å thick. a) P-polarized light, incidence angle 85°. b) Un-polarized light, incidence angle 45°.

The carbonyl stretching frequency at  $1725\text{ cm}^{-1}$  and the out of plane aromatic ODA  $\nu_{13}$  mode at  $1505\text{ cm}^{-1}$  both have a dynamical dipole moment perpendicular to the chain axis of the polymer. As schematically shown in Fig. 4, the polyimide chain is not straight, but due to the bond angle in the ODA molecules exhibits a "zig-zag" orientation. Russell [29] reported x-ray diffraction data on spun-on polyimide films, from which he concluded that the polyimide chains are oriented parallel to the surface. However, from his data, which give the projection of the polyimide repeat unit onto the surface plane, it cannot be determined whether the "zig-zag" structure is in the plane or perpendicular to the plane of the surface. Since the vibrational modes which have a dynamical dipole along the chain axis are intense in the p-polarized spectra, we have to conclude that the direction of the chains must have a component perpendicular to the surface, which is the case for a zig-zag orientation perpendicular to the substrate as indicated in Fig. 4. When both polarizations of the light contribute to the spectrum (3b), the relative intensity ratio between the out of plane modes (with respect to the polymer chain) and the axial modes changes. It appears that the out of plane modes ( $\nu_{CO}$ ,  $\nu_{13}$ ) are more intense due to the additional s component of the light. The dynamical dipole moment of the  $\nu_{CO}$  mode and the  $\nu_{13}$  phenyl modes are close to perpendicular to each other due to the staggered configuration of the ODA and PMDA constituents of the chain. Yet the intensity ratio between these two bands does not change as a function of polarization, which means that both the PMDA and ODA moieties must be inclined by approximately the same angle with respect to the surface normal. Such a configuration would result in a polarization independent absorption ratio of these two

be 1s and an equal enhancement of absorption when the light is unpolarized. Since the polymer chains will have random azimuthal orientation in the configuration shown in Fig. 4, the intensity ratios between the axial modes will be largely independent of both polarization and incidence angle as observed experimentally.

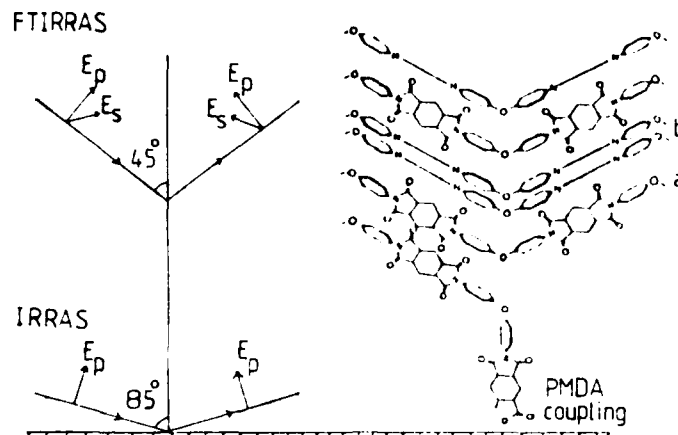


Figure 4. Orientation of the polyimide chains as determined from the infrared reflection absorption data. The polyimide chains are oriented parallel to the surface, the "zig-zag" of the chains is on average in the plane of the surface normal. The orientation of the PMDA and ODA units is in between the two orientations labelled a and b. Chemical bonding to the substrate is indicated by a PMDA fragment adsorbed on a silver surface.

Our IR data thus supports the orientational model shown in Figure 4 where the rotational orientation of ODA and PMDA units of the chains with respect to the polymer axis must be between the two structures indicated as a and b.

In Figure 4 we also show the postulated interlink between the polyimide film and a PMDA fragment on a silver surface. This model is consistent with our previous XPS and NEXAFS data for PMDA adsorbed on silver and with the infrared absorption data described above.

#### Topographic Changes in Thin Polyamic Acid Films During Imidization

During imidization of the polyamic acid the average thickness of the film decreases by up to 60% [20,23,24], due to loss of material and structural changes in the film. XPS results on the ultra thin polyimide ( $d < 40$  Å) films on silver, copper and gold further revealed that the film must become discontinuous.

To study these topographical changes we have used a Digital Instruments Nanoscope I to obtain scanning tunneling microscope (STM) images of polyimide films at various stages during curing. Figure 5 shows two examples. In this case the substrate is a gold film evaporated onto mica. The codeposited PMDA-ODA film was heated in vacuum below the imidization temperature (390 K for 15 minutes) (Fig. 5a) and then was cured at 425 K in vacuum for 15 minutes (Fig. 5b). After each heating, the film was removed for examination by STM and FTIR. The uncured film (Fig. 5a) was about 100 Å thick based upon attenuation of the gold XPS signals. The area shown in the STM images is about 200 Å by 180 Å and the topographic relief in 5b is about 5 Å. The uncured film shows no topographic features, the apparent structure in the pho-

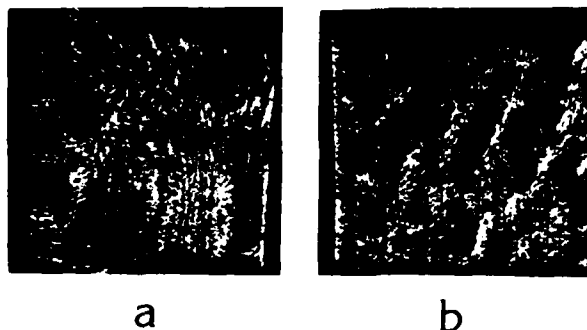


Figure 5. Scanning tunneling micrographs of (a) a thin polymer film (100 Å thick) on a gold substrate and (b) for the same film partially imidized at 425 K for 15 minutes. The regions depicted are 200 Å x 180 Å. The ridges are about 35 Å apart and the relief in surface topography is about 1 Å. The tunneling current was about 2 nA.

graph is due to Moiré' interference on the oscilloscope screen of the image. In the partially cured film, however, the graphical features consist of ten parallel ridges spaced about 35 Å, and it is possible to observe changes for the detailed local structure varies in the film. The film structure is not coherent across the region of the image. Again, the STM image (Fig. 5b) supports the structural model shown in Fig. 4. A comparison of the STM images taken before and after imidization then demonstrate that the structural changes in the polymer film also induce topographic changes.

#### SUMMARY

Our XPS and IR studies show that the two polyimide constituents undergo partial fragmentation on silver and copper surfaces. In the case of PMDA the interaction with the substrate is dominated by the anhydride functionality. In the case of ODA a less specific interaction seems to occur. The interfacial PMDA fragment retains its ability to interact with oxidianiline and the ODA fragments can also act as a chemical interlink is at present not clear.

Imidization of the vapor phase deposited polyamic acid results in a structural change of the polymer chains with respect to the surface, which in turn causes topographical changes in the film surface. In the cured polyimide film, the polymer chains are in average oriented parallel to the surface, with their "zig-zag" structure having a strong component in the direction of the surface normal.

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